# Molecular Orientation in Polymer Foams Determined Using STXM

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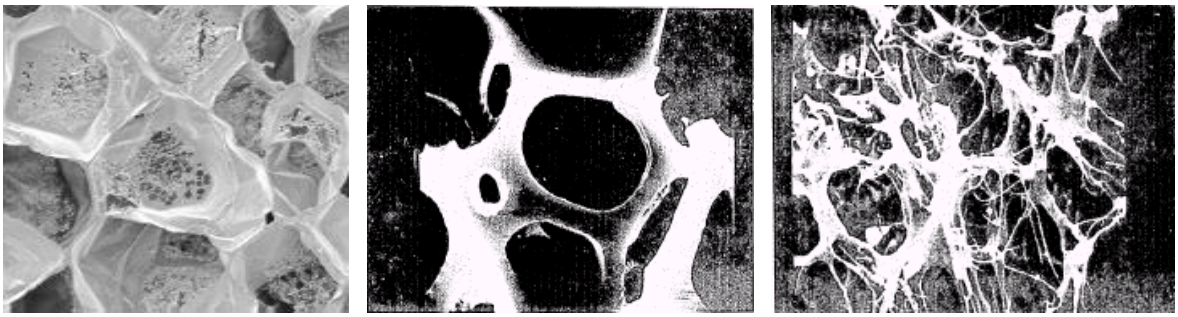
## INTRODUCTION

The method for producing extruded thermoplastic polymer foams involves mixing a molten polymer and blowing agent under high pressure to maintain a single phase and expanding this into a reduced pressure environment. When the blend is extruded, the rapid decompression causes the nucleation and phase separation of blowing agent. The bubbles, which form, expand and the foam structure stabilizes as the polymer matrix solidifies, locking in the foam morphology. It is possible to producing foam with cell morphologies ranging from closed to open cell structures. Open cell foams can have holes in the windows, have the windows fully open with only struts remaining connected or the struts may even be broken as in fibrillated foams known in cigarette filter applications. Figure 1 shows SEM micrographs of the cellular morphologies of various open cell polypropylene foams. The type of foam structure and the final properties (strength, density and insulating properties) of the foam are determined by the chemistry, and the process parameters, such as, extrusion rate, amount of blowing agent, cooling rate, and the foaming temperature and pressure. The final foam attributes can vary from brittle to soft and from friable to resilient, by the control of cell structure and the induced orientation.

The key factors affecting the molecular orientation in the foam, is the rate of expansion and the distribution of polymer into walls or struts. However, the local temperature and rate of cooling that are critical to determining the final foam microstructure, are difficult to measure accurately. We have been investigating the use of scanning transmission x-ray microscopy (STXM) to ascertain the local degree of molecular orientation in polypropylene foams. Since the amount of expansion and the rate of cooling determine the degree of molecular orientation of the polymer, measurement of the orientation should provide clues to the local temperature and rate of cooling during manufacture and thus provide guidance in processing modifications to achieve the desired foam properties.



1a 1b 1c

Figure 1. SEM micrographs of open cell foams illustrate the range of cell morphologies. Fig.1a shows open cell PP with pores in the window [1]. Fig. 1b and 1c show respectively, open cell PP having the windows fully opens, and open windows with the struts broken as described in reference [2].

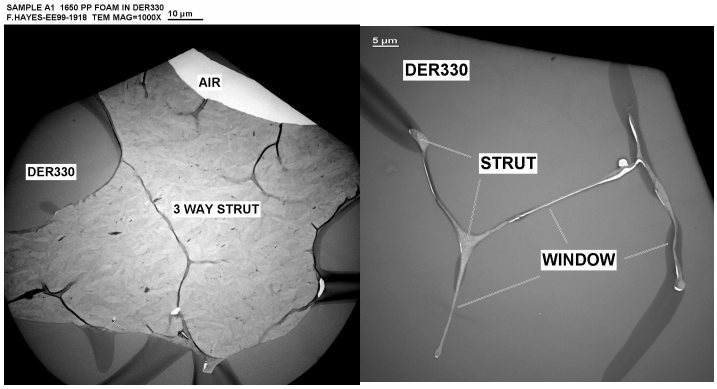



Figure 2. TEM images of thin sections of two different polypropylene foams to illustrate the range of shapes for windows and struts. The phase marked DER330 refers to the epoxy used to embed the foams for microtomography.

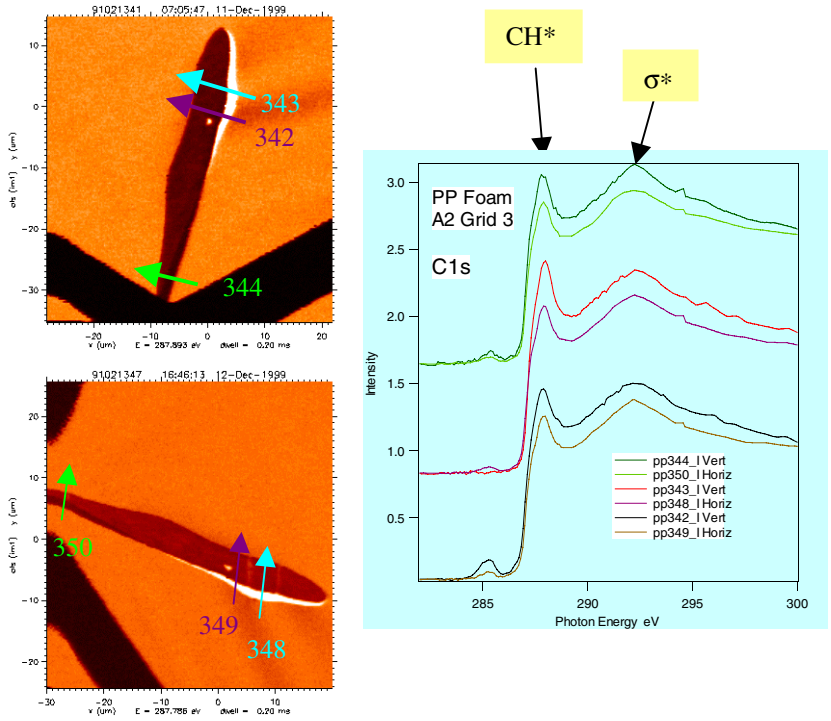
**EXPERIMENTAL**

Foams were produced as rods using various processing condition. Samples of various foams were prepared by embedding them in (DER330) epoxy and using an ultramicrotome to cut thin sections (~ 100 nm thick) through the foam and the epoxy. Figure 2 shows TEM micrographs of examples of two different thin sections. The windows are the walls of the individual cells and the struts occur at the intersection of the windows. In the two-dimensional thin sections shown in Figure 2 the struts connect three windows. Similar samples were examined with the Beamline 7.0.1 STXM.

The STXM analyses were performed using the microscope on beamline BL 7.0.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory. This facility has been described previously [3]. Spectra were acquired using the line scan mode wherein a single line is repeatedly scanned at a series of different energies and spectra are thus recorded from each point on the line. Some realignment of the line scans is accomplished in software to minimize errors due to pointing errors. In order to increase the signal to noise ratio, data from several adjacent points can be summed, being careful not to include data from points on the surrounding epoxy.

**RESULTS**

Line scan STXM spectra were acquired for windows and struts, taking care to align the windows vertically and horizontally relative to the (horizontal) orientation of the photon electric vector. Not surprisingly, the windows were found to be much more oriented than the struts. The windows undergo much more strain during the expansion process than do the struts consistent with the higher orientation. The center of the struts should be essentially stress free and thus isotropic. Example data are provided in Figure 3 for foam with open cells. The strut is not visible in the images on the left-hand side of the Figure, but the locations where three different spectra were obtained on the window are indicated. The spectra obtained from linescans are compared in the graph in the middle of the Figure. The resultant peak intensities and ratios of peak intensities are compared in the Table at the right-hand side of the Figure. These results are complicated by the need to understand the relationship of the transition dipole moment to the molecular axis. It appears from the results that the peak labeled CH* should be oriented approximately perpendicular to the molecular axis, and the peak labeled $\sigma^*$ also appears to be so polarized, though to less of an extent. To date results which have been obtained from struts are always less oriented than windows and windows




| File | Orient | C-H | σ* | C-H ratio | σ* ratio |
|---|---|---|---|---|---|
| 342 | vert | 1.46 | 1.50 | 1.17 | 1.09 |
| 349 | horiz | 1.25 | 1.38 | | |
| | | | | | |
| 343 | vert | 1.61 | 1.54 | 1.27 | 1.13 |
| 348 | horiz | 1.28 | 1.36 | | |
| | | | | | |
| 344 | vert | 1.46 | 1.53 | 1.16 | 1.15 |
| 350 | horiz | 1.25 | 1.34 | | |
| | | | | | |
| | | | Avg. | 1.20 | 1.12 |
| | | | σ | 0.06 | 0.03 |

Figure 3. Example STXM images of an open-celled foam, indicating the location from which line scan spectra were obtained (right), comparison of the spectra in the graph at center, and comparison of relative band intensities and ratios of band intensities for these same data, in the table at the right.

which are from lower density foams exhibited higher spectral anisotropy. This work is still in an early phase. Future work will be performed to calibrate the spectral anisotropy to polymer orientation and use these relationships to compare and provide a clue to the relative rate of cooling and differences in local foaming temperatures for foams made in different ways.

**CONCLUSIONS**

STXM experiments have been initiated to understand the relationship of polymer orientation at the microscopic level in polymer foams. The initial experiments showed that STXM is sensitive to orientation in the foam windows. The observed spectral anisotropy correlated with expected trends, in terms of struts lower than windows and more highly expanded foams exhibited higher anisotropy.

**REFERENCES**

1. Daniel Imeokparia et al., US Patent #5411687
2. Samuel Baxter et al., US Patent #4232130
3. T. Warwick, K. Franck, J.B. Kortwight, G. Meigs, M. Moronne, S. Myneni, E. Rotenberg, S. Seal, W.F. Steele, H. Ade, A. Garcia, S. Cerasari, J. Denlinger, S. Hayakawa, A.P. Hitchcock, T. Tyliszczak, E.G. Rightor, H.-J. Shin and B. Tonner, *Rev. Sci. Inst.* **69,** 2964 (1998) .

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